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(54) [Title of the invention] Polymer electrolyte film and production method therefor

(57) [Abstract]

[Constitution] Polymer electrolyte film comprising polymer porous film prepared by drawing and ion exchange resin that is contained in at least the pores of said porous film.

[Advantages] The prevention of damage to the polymer electrolyte film caused by the repeated swelling and shrinking of the ion exchange resin during the operation of the device in which the polymer electrolyte film is fitted, prolongation of the life of the polymer electrolyte film, and the resulting prolongation of the life of the solid polymer fuel cell, aqueous electrolysis device or the like in which the polymer electrolyte film is fitted.

[Scope of the patent claims]

[Claim 1] A polymer electrolyte film comprising polymer porous film prepared by drawing and ion exchange resin that is contained in at least the pores of said porous film.

[Claim 2] A method for the production of a polymer electrolyte film, characterised in that polymer porous film prepared by drawing is impregnated with ion exchange resin solution, then the solvent is removed.

[Detailed description of the invention]

[0001]

[Field of industrial use] The present invention relates to a polymer electrolyte film for use in solid polymer fuel cells, aqueous electrolysis devices and the like, where said polymer electrolyte film is not damaged by repeated changes in the device operating conditions; and to a production method therefor.

[0002]

[Prior art] The demand for an improvement in the energy efficiency of polymer electrolyte films used for solid polymer fuel cells, aqueous electrolysis devices and the like has necessitated a decrease in the film resistance of the polymer electrolyte film, and there have therefore been attempts to decrease the film thickness. However, when the film is made thinner, its strength inevitably decreases, and so the electrolyte film breaks when it is incorporated into solid polymer fuel cells or aqueous electrolysis devices, or the film tears after incorporation as a result of the difference in pressure either side of the film, or the sealed parts around the circumference of the film split.

[0003] In order to prevent such damage, Japanese examined patent H1-57693 suggests a polymer electrolyte film and technology for the production thereof involving a method whereby ion exchange resin is embedded in woven cloth.

[0004]

[Problem to be overcome by the invention] Conventional polymer electrolyte films obtained using woven cloth or the like as reinforcing material are disadvantageous in that separation occurs at the interface between the woven cloth fibres and the ion exchange resin, with the result that the ion exchange resin drops out and holes open up in the polymer electrolyte film, and so forth.

[0005] The cause of this is thought to be as follows. The ion exchange resin swells and shrinks as its water content varies. Moreover, the woven cloth used as the

reinforcing material for the polymer electrolyte film works to inhibit the swelling and shrinking of the ion exchange resin, which adds stress at the interface between the fibres of the woven cloth and the ion exchange resin. Consequently, in devices in which the operating conditions (output, etc.) change repeatedly, such as aqueous electrolyte devices, solid polymer fuel cells and the like, the repeated generation of the abovementioned stress is thought to bring about release at the interface.

[0006]

[Means of overcoming the problem] The present inventors perfected the present invention as a result of continued investigation into the development of a polymer electrolyte film that is not damaged even when the ion exchange resin water content changes repeatedly. The present invention is, in essence, a polymer electrolyte film comprising polymer porous film prepared by drawing and ion exchange resin that is contained in at least the pores of said porous film, and a method for the production of polymer electrolyte film, characterised in that polymer porous film prepared by drawing is impregnated with ion exchange resin solution, then the solvent is removed.

[0007] The polymer porous film used in the present invention is prepared as follows. Fluorine resin (for example, polytetrafluoroethylene or the like) or another resin (such as polypropylene, polyethylene or the like) is drawn at least uniaxially at a temperature no greater than the crystal melting point, as in Japanese examined patents S42-13560 and S51-18991, then heated at a temperature no lower than the crystal melting point while still in a drawn state, to obtain the polymer porous material of a three-dimensional network structure used in the present invention. The porous film used in the inventive polymer electrolyte film is preferably of a thickness of from 10 to 200  $\mu\text{m}$ , preferably has an average pore size of from 0.1 to 10  $\mu\text{m}$ , and preferably has a porosity of from 50 to 95%.

[0008]

[Use] By using polymer electrolyte film comprising polymer porous film prepared by drawing and ion exchange resin that is contained in at least the pores of said porous film, it is possible to prevent the damage to the polymer electrolyte film caused, for example, by repeated changes in operating conditions during operation of the device. The reason for this is not absolutely clear, but is thought to be as follows.

[0009] Polymer porous film that has been prepared by drawing has a three-dimensional network structure and therefore has elasticity in any direction. Consequently, polymer electrolyte film comprising polymer porous film prepared by

drawing and ion exchange resin that is contained in at least the pores of said porous film expands and contracts with the swelling and shrinking of the ion exchange resin, with the result that separation at the interface between the ion exchange resin and the polymer porous film tends not to occur, and damage to the polymer electrolyte film is prevented.

[0010] Furthermore, when a porous film that has been prepared by biaxial drawing is used, more of a three-dimensional network structure is obtained, and so polymer porous [sic] film comprising polymer porous film prepared by biaxial drawing and ion exchange resin that is contained in at least the pores of said porous film undergoes more expansion and contraction with the swelling and shrinking of the ion exchange resin, making separation at the interface between the ion exchange resin and the polymer porous film even less likely, and thereby affording greater prevention of damage to the polymer electrolyte film.

[0011] The inventive polymer electrolyte film is preferably prepared by impregnating the polymer porous film with ion exchange resin solution, then drying, to fix the ion exchange resin in the polymer porous film. The solvent should be selected according to the type of ion exchange resin; for example, when perfluorocarbonsulfonic acid is used, as in the examples, it is preferable to use isopropanol or the like as solvent.

[0012] The concentration of the ion exchange resin in the solvent is usually from 1 to 5%. If the concentration is too low, the impregnation and drying process has to be repeated in order to impregnate the polymer porous film with the necessary amount of ion exchange resin, whereas if the concentration is too high, the viscosity of the solution increases, with the result that the impregnation operation becomes problematical and the solution does not adequately penetrate to within the porous film.

[0013] The drying temperature should be selected as appropriate depending on the type of solvent, and the drying can be performed under reduced pressure if necessary.

[0014] The amount of ion exchange resin in the polymer porous film after drying is from 1 to 100 g, preferably from 10 to 40 g, per g of porous film.

[0015]

[Examples]

Example 1

(I) Porous film (average pore size 1  $\mu\text{m}$ , film thickness 50  $\mu\text{m}$ , porosity 90%) prepared by drawing polytetrafluoroethylene was impregnated with a 5% by weight

isopropyl alcohol solution of perfluorocarbonsulfonic acid (Nafion (registered trademark), DuPont) (Aldrich Chemicals), and the system was dried at 60°C. (II) Next, the film was be treated for 5 minutes at 140°C. Operations (I) and (II) were repeated until there were no pinholes (5 times).

[0016] The resulting film was immersed in 1N sulphuric acid at from 60 to 70°C for 1 hour, then immersed in pure water at from 60 to 70°C for 1 hour, to exchange the ion exchange resin side-chain terminal groups with  $-\text{SO}_3\text{H}$ .

[0017] Comparative example 1

25 mesh gauze fabric comprising 200 denier polytetrafluoroethylene multifilament as the weft and 200 denier polytetrafluoroethylene multifilament as the warp was used as the reinforcing woven cloth. (I) This reinforcing woven cloth was impregnated with 5% by weight Nafion solution (manufactured by Aldrich Chemicals), then dried at 60°C. (II) Next, it was heat treated for 5 minutes at 140°C. Operations (I) and (II) were repeated until there were no pinholes and the film thickness was 50  $\mu\text{m}$  (5 times). No pinholes were seen.

[0018] This film was immersed in 1N sulphuric acid at from 60 to 70°C for 1 hour, then immersed in pure water at from 60 to 70°C for 1 hour, to exchange the ion exchange resin side-chain terminal groups with  $-\text{SO}_3\text{H}$ .

[0019] The films obtained in Example 1 and Comparative example 1 were each subjected to a "swelling cycle test". After the test, no pinholes were seen in the Example 1 film, although pinholes had developed in 20% of the Comparative example 1 film.

[0020] The "swelling cycle test" was performed as follows. The polymer electrolyte film was cut into a disc of a diameter of 6 cm, an O-ring was placed on the outer part (diameter 5 cm) and sandwiched from above and below using a donut-shaped weight, the weight was fixed in 6 places using nuts and bolts, and the system was immersed in pure water at 90°C for 5 minutes, then taken out and dried at 100°C for 5 minutes. This immersing and drying process was repeated 10 times, then the system was inspected visually for holes due to ion exchange resin dropout, and then pressure was applied from one side of the film and the system was observed for air leakage from the other side, and the presence or absence of pinholes was appraised.

[0021]

[Advantages of the invention] The inventive polymer electrolyte film affords prevention of the damage to the polymer electrolyte film caused by the repeated

swelling and shrinking of the ion exchange resin during the operation of the device in which the polymer electrolyte film is fitted. It is therefore advantageous for use in the field of solid polymer fuel cells, aqueous electrolyte devices and the like.